

SEASON 2 - 2021 2022

REACTIVE MERCURY IN AIR



This online webinar will look into how atmospheric mercury monitoring can support the Minamata Convention – policy making, implementation and evaluation. This event will focus on comparability of measurements of the three forms of atmospheric mercury: gaseous elemental (GEM), gaseous oxidized (GOM), and particulate bound (PBM). Currently, comparability of GEM can be demonstrated, while limited metrological infrastructure for traceable, validated, and accurate measurements of oxidized mercury species in the atmosphere exists.





Please register for the WebEx session using the link above. Information about Minamata Online Check the Season 2 calendar

SPEAKERS



Mae Sexauer Gustin University of Nevada, Reno



Seth Lyman Utah State University

Reno



Reno Lynwill Martin International Conference on Mercury as a Global Pollutant



Eisaku Toda Senior Policy and Coordination Officer



Milena Horvat Jožef Stefan Institute, Slovenia

Sarrah Dunham-Cheatham University of Nevada,



Iris de Krom National Metrology Institute, The Netherlands

MERCURY SCIENCE

Housekeeping notes



- You may wish to test (and adjust) your speaker and microphone settings by opening the Audio & Video menu at the top-left corner of your screen.
 File Edit Share View Audio & Video
- You can open the Participants panel and the Chat panel by clicking the respective icon at the bottom-right corner of your screen.
- You may wish to type question(s) in the chat box and send to "everyone".
- If you need any technical assistance, please put your message in the chat box and send it to the 'host'.
- Kindly note that this session is recorded and broadcasted. Recording of this session and the presentation slides will be made available through the Minamata Convention website after the session.

$Q_{=}$ Participants	C Chat	

MINAMATA CONVENTION ON MERCURY

The Parties to this Convention,

Recognizing that mercury is a chemical of global concern owing to its long-range atmospheric transport, its persistence in the environment once anthropogenically introduced, its ability to bioaccumulate in ecosystems and its significant negative effects on human health and the environment,

Recalling decision 25/5 of 20 Fe of the United Nations Environmen action to manage mercury in an effi





UN @

GLOBAI

Article 1 Objective



The objective of this Convention is to protect the human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds.





Article 19 Research, development and monitoring

1. Parties shall endeavour to cooperate to develop and improve, taking into account their respective circumstances and capabilities:

(a) Inventories of use, consumption, and anthropogenic emissions to air and releases to water and land of mercury and mercury compounds;

(b) Modelling and geographically representative monitoring of levels of mercury and mercury compounds in vulnerable populations and in environmental media, including biotic media such as fish, marine mammals, sea turtles and birds, as well as collaboration in the collection and exchange of relevant and appropriate samples;

(c) Assessments of the impact of mercury and mercury compounds on human health and the environment, in addition to social, economic and cultural impacts, particularly in respect of vulnerable populations;

(d) Harmonized methodologies for the activities undertaken under subparagraphs (a), (b) and (c);

(e) Information on the environmental cycle, transport (including long-range transport and deposition), transformation and fate of mercury and mercury compounds in a range of ecosystems, taking appropriate account of the distinction between anthropogenic and natural emissions and releases of mercury and of remobilization of mercury from historic deposition;

Article 22 Effectiveness evaluation

1. The Conference of the Parties shall evaluate the effectiveness of this Convention, beginning no later than six years after the date of entry into force of the Convention and periodically thereafter at intervals to be decided by it.

2. To facilitate the evaluation, the Conference of the Parties shall, at its first meeting, initiate the establishment of arrangements for providing itself with comparable monitoring data on the presence and movement of mercury and mercury compounds in the environment as well as trends in levels of mercury and mercury compounds observed in biotic media and vulnerable populations.

3. The evaluation shall be conducted on the basis of available scientific, environmental, technical, financial and economic information, including:

(a) Reports and other monitoring information provided to the Conference of the Parties pursuant to paragraph 2;

(b) Reports submitted pursuant to Article 21;

(c) Information and recommendations provided pursuant to Article 15; and

(d) Reports and other relevant information on the operation of the financial assistance, technology transfer and capacity-building arrangements put in place under this Convention.





NERCUR

SSESSMENT

Figure 8.2 Observed and modelled trends for 1990 to 2013 in atmospheric gaseous elemental Hg concentrations (upper four plots) and divalent Hg^{II} wet deposition fluxes (lower two plots) in different regions of the Northern Hemisphere. Observations for individual years are shown as squares with linear regression as a solid line. The dashed line is the trend from the GEOS-CHEM simulation using the revised anthropogenic emissions inventory for 1990 and 2010. The data are averaged regionally across the free troposphere, North America, Western Europe, and high northern latitude regions. From Zhang et al. (2016c).

Figure 4.2 Hemispheric gradient in GEM concentration for GMOS data in 2013 and 2014. Sites are organized by latitude. For each box the midline indicates the median, the box indicates the 25th and 75th percentiles, and the whiskers indicate the 5th and 95th percentiles (Sprovieri et al., 2016).

Reactive Mercury in Air



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Programme

- Lynwill Martin: Guidelines for mercury monitoring for effectiveness evaluation air
- Iris de Krom: Comparability of the measurement results for gaseous elemental mercury
- Mae Sexauer Gustin, Milena Horvat, Seth Lyman, Sarrah Dunham Cheatham: Practical demonstration of oxidized mercury measurements: sampling artefacts and calibration
- Discussion: moderated by Milena Horvat
- Closing Minamata Convention Secretariat and ICMGP



CCNGP MERCURY AS A GLOBAL POLLUTANT 24TH - 29TH JULY 2022 VIRTUAL EVENT

REDUCING MERCURY EMISSIONS TO ACHIEVE A GREENER WORLD



www.ilmexhibitions.com/mercury2022/



MER 24TH VIRTI

GMG

ACHIEVE A GREENER WORLD

REDUCING MERCURY EMISSIONS TO

EXECUTIVE COMMITTEE



Dr Lynwill Martin Chairperson: Conference



Dr Joy Leaner Co-Chairperson: Conference

Prof Vernon Somerset Co-Chairperson: Scientific Committee



Dr Chavon Walters Co-Chairperson: Local Organising Committee



Ms Maria Cuoto



Prof Ralf Ebinghaus



Prof Robert Mason



Mr Marcus Pattison



Mr Rico Euripides





Dr Alexandra (Sandy) Steffen



Prof Dr Jozef Pacyna



Assoc Prof Asif Qureshi



MER 24TH VIRTI

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REDUCING MERCURY EMISSIONS TO

LATEST NEWS | CALLS:



Announcing the ICMGP 2022 - Katherine Mahaffey Lifetime Achievement **Award Winner**

On the behalf of the mercury scientific community, the Executive Committee and Scientific Steering Committee of the 15th International Conference on Mercury as a Global Pollutant, cordially congratulate Professor Robert Mason for receiving the Katherine Mahaffey LAA Award. ... Read More



Call for papers on Mercury Research

The Scientific Committee of ICMGP The 15th International Conference on Mercury as a Global Pollutant have announced a Call for Papers. The 2022 ICMGP conference will be held virtually from the 24th-29th July. Being held virtually will now give more access and opportunities for Mercury Researchers ... Read More

Extended until 15 March

https://www.ilmexhibitions.com/mercury2022/



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REDUCING MERCURY EMISSIONS TO

LATEST NEWS | CALLS:

Week of 18 – 22 July

ICMGP Workshops (13) ASGM, Coding, Arctic ect. Topic on Reactive Mercury Measurement will be presented also by Mae Gustin & Team

Week of 24 – 29 July Plenary Talks

Mon: Global Change and Biogeochemical Mercury Cycling Health day Tue: Minamata Storyteller (Setting the Scene) Correct use of Hg Guideline Values by Non-health Experts Wed: Next Gen – Future of Mercury Research at a Glance Thu: Industrial Emissions and Challenges



LATEST NEWS | CALLS:

24 March

5th Scientific Steering Committee Meeting (Abstracts)

Registration to open middle April

REDUCING MERCURY EMISSIONS TO ACHIEVE A GREENER WORLD **C**MG

Guidelines for mercury monitoring for effectiveness evaluation

Reasoning Behind the Document

Lynwill G Martin

Aim & Process of Monitoring Guidance

- (i) explain the role of monitoring in the effectiveness evaluation and set realistic expectations about what can be learned over time;
- (ii) provide guidance to parties and organizations that are currently conducting monitoring programmes on what data and accompanying information would inform the effectiveness evaluation; and
- (iii) provide guidance to parties and organizations who wish to develop new monitoring programmes or improve existing ones, with a view to contributing to the effectiveness evaluation.



Process

Guidance: Lead Author Team

- Executive summary Manoela Miranda, UN Environment Programme
- Atmospheric mercury monitoring Lynwill Martin, South African Weather Service
- Biota mercury monitoring David Evers, *Biodiversity Research Institute*
- Human biomonitoring Nil Basu, McGill University
- Cross-media data analysis Colin Thackray, Harvard University
- Supplementary material:
- Part A: monitoring programmes and SOPs
- Part B: QA&QC procedures and draft template

Setting the Stage – Chapter 2

Tiered approach:



Tier 3: Basis for understanding key processes that link sources to environmental concentrations and exposures

Tier 2: Basis for assessing source attribution at the local, national, and global scales. Methods may be more expensive or complex (Research)

Tier 1: Limited set of parameters. Methods are cost effective, practical, feasible, and sustainable

Chapter 3: Why Atmospheric Mercury Monitoring

- Minamata Convention Article 1 = "protect human health & Environment"
- Reports by AdHoc Experts Group Highlights Air as a suitable matrix to help evaluate the Convention's effectiveness
- Mercury is a naturally occurring element and is emitted to the atmosphere from a variety of sources
- There are three forms or species/fractions of mercury commonly found and measured in the atmosphere:
 - Gaseous elemental mercury (GEM)
 - Gaseous oxidized mercury (GOM)
 - Particle-bound mercury (PBM)

REACTIVE MERCURY (RM)

- GEM/TGM Measurements well established and good comparability achieved already
- Uncertainty associated with commercially available Speciation Unit for RM measurement satisfactory results obtained during comparison (AMNet & Can) but room for improvement

Why are we interested in measuring RM for EE

- Atmospheric RM is meaningful to reveal the behaviors of regional atmospheric mercury cycles and identify the contribution of local or regional emission sources
- RM measurements also provide valuable information e.g help evaluate models
- It's important as they help to improve the understanding of short-term oxidation processes regarding the removal of mercury from the atmosphere
- Monitoring of RM for EE makes sense only if there is a universally agreed upon, reliable, and accurate method for it. (New studies/research)









Why Use a Tiered Approach?

With over 135 Parties that have ratified the MC, fewer than 20% of countries have an Air Monitoring Program that is currently active

Guidance looks at the following:

- Parties with no monitoring activities
- Parties that use one method of sampling (e.g., wet deposition in APMMN)
- Parties that have two or more techniques of Hg air monitoring
- Parties that have well established network of stations and can do advance research or Hg monitoring

Tiered approach is the best way to meet all Parties Needs that no Party is left behind in Making Mercury History

Why Use a Tiered Approach?

Monitoring category	Observation Data	Metadata	Ancillary Data	Analyses
Air - Tier 1	TGM and GEM levels; Wet deposition The measurement methods cost effective , practical , feasible, and sustainable. Automated, Manual , Passive , wet deposition methods	Latitude; longitude; elevation; Sampling time, frequency, duration; averaging methods; sampling method	Measurement/method uncertainty; proximity to known point sources; type (urban/regional/background); meteorological variables;	 Temporal trends Atmospheric model evaluation (for GEM) Spatial variations Input for local-scale modelling Back-trajectory analysis Bottom-up attribution analysis
Air - Tier 2	Air - Tier 1 and High-resolution PBM and GOM; Estimates of dry deposition of mercury (using concentrations and site specific deposition velocities); mercury throughfall	Air - Tier 1	Air - Tier 1 and deposition of Sulfate; Land Cover; Land Use; Leaf Area Index; Air Quality Tracers (e.g., SO ₂ , CO ₂ , CO, PM _{2.5} , O ₃)	 Air - Tier 1 and Estimate air-ocean and air- terrestrial mercury exchange Covariate profiling Top-down attribution analysis
Air - Tier 3	Air - Tier 2 and mercury isotopes; Measurements of dry deposition; additional speciation measurements Speciation Measurement with new techn Prototype Equipment	Air - Tier 2 Niques	Air - Tier 2	 Air - Tier 2 and Combined "top-down" and "bottom-up" attribution analyses Isotopic fingerprinting

Source: UNEP/MC/COP.4/INF/12

Tier 2 & 3 Monitoring Provides Opportunity for RM...

- New research to investigate these findings that could help the Convention on monitoring to maintain harmonized, comparable information on mercury levels in the environment **Decision BS-3/10**
- Article 19 focus on Research Development and Monitoring
- Following talks will highlight this current/new research approach of improving our understanding of RM measurements





The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Comparability of the measurement results for gaseous elemental mercury (GEM)

Iris de Krom – National Metrology Institute – VSL

1 March 2022 – Minamata online



Importance of measurements











Nationa

VSL Metrological traceability

- Metrology is the <u>science</u> of <u>measurement</u>. Metrology includes all theoretical and practical aspects of measurement.
- Traceability is the ability to verify the history, location, or application of an item by means of documented recorded identification. ("Trackability")
- The term "metrological traceability" is used to refer to an unbroken chain of comparisons relating an <u>instrument</u>'s <u>measurement results</u> to a known measurement <u>standard</u>.















VSL National metrology institutes

Aim

- Knowledge of national metrological structure
- Subjects
 - Système International (SI)
 - Measurement standards
 - Developments
 - Key Comparisons









L Traceability of gaseous elemental mercury

- EMRP ENV02 PartEmission (2010 2013)
- EMRP ENV51 MeTra <u>http://projects.lne.eu/metra/</u> (2013 2016)
 - Development of traceable calibration methods for mercury
- EMPIR 16ENV01 MercOx <u>http://www.mercox.si/</u> (2017 2020)
 - Development of traceable calibration methods for oxidised mercury
- EMPIR 19NRM03 SI-Hg <u>http://si-hg.eu/</u> (2020 2023)
 - Metrology for traceable protocols for elemental and oxidised mercury concentrations













SL Primary Mercury Gas Standards

- Gaseous Elemental Mercury \rightarrow GEM
- Traceable to SI-units
- Uncertainty

VSL – diffusion method
 de Krom et al. Measurement 169 (2021) 108351
 doi: <u>https://doi.org/10.1016/j.measurement.2020.108351</u>
 de Krom et al. Atmos. Meas. Tech., 14 (2021) 2317
 doi: <u>https://doi.org/10.5194/amt-14-2317-2021</u>

NIST – spectroscopy
 Srivastava et al. Anal. Chem. 90 (2018) 6781
 Doi: <u>https://doi.org/10.1021/acs.analchem.8b00757</u>
 Srivastava et al. Anal. Chem. 93 (2020) 1050
 Doi: <u>https://doi.org/10.1021/acs.analchem.0c04002</u>





National Metrology Institute elemental mercury (GEM)

Comparability of the measurement results for gaseous

SI traceable reference materials

VSL gas generator & NIST SRM (3133)

Field method

Dumarey equation







8-11-2022

VSL

National

Metrology Institute



VSL Traceability for elemental mercury measurement results

- Traceability for gaseous elemental mercury (GEM)
 - In emission sources and the atmosphere
 - Comparisons between current calibration facilities
 - Dumarey equation
 - NIST SRM
 - Calibration services
- Future

National

Metrology Institute

- SI traceability in written standards
- Unbroken chain of mercury measurement results from primary standards to industry and monitoring programmes



Contact Info: Iris de Krom idekrom@VSL.nl www.SI-Hg.eu

Practical demonstration of oxidized mercury measurements: sampling artifacts and calibration

Mae Sexauer Gustin^{1,*}, Seth Lyman², Sarrah M. Dunham-Cheatham¹, Milena Horvat³

¹ University of Nevada, Reno, Reno, Nevada, USA
 ² Bingham Research Center, Utah State University, Vernal, Utah, USA
 * <u>mgustin@unr.edu</u>

³Jožef Stefan Institute, Ljubljana, Slovenia







Scientific understanding evolves over time

Progress is made as

- Our knowledge increases
- \circ Our methods improve



Oxidized Hg



Why is it important to measure?

- Emitted from point sources at high concentrations
- $\,\circ\,$ Also present in the air we breathe, or "ambient air"
 - Derived from:
 - Point sources
 - Chemical reactions in the atmosphere with Hg⁰
 - Emissions from natural sources

Here, we will focus on **ambient atmospheric** measurements, not emission measurements



Oxidized Hg Measurement Challenges

Difficult to measure

- o "Sticky"
- \circ Reactive
 - Can be reduced to elemental Hg⁰ depending on atmospheric chemistry
- Low concentrations (low parts-per-quadrillion)

Methods to measure have evolved over time

- First used manual denuders for GOM and filters for PBM
- Tekran, in collaboration with others, developed an automated system for operationally defined GOM and PBM measurements





Common Methods

Preconcentration methodologies:

- GEM (Hg⁰): gold traps, AC traps, oxidizing solutions Ο
- GOM (Hg²⁺): KCl denuders/sorbent traps/impingers, ion exchange membranes Ο



	denuders	
[sorbent traps	
	membrane traps)



Tekran[®] System

Being used in networks world-wide

High uncertainty associated with GOM and PBM measurements

 GOM measurement is biased low by 2- to 13times

No ambient air field calibration for GOM nor PBM





Need for New Methods & Calibration

Over the past 10 years, it has become clear the Tekran GOM and PBM measurements are impacted by the chemistry of the atmosphere

- New accurate methods for GOM and PBM measurement need to be developed
- Calibration traceable to an international standard is needed
 - $\circ~$ Achieving oxidized Hg calibration is not a minor task
 - Global community has been working on this for a decade
 - Need of in **SI traceable** and/or **globally** agreed calibration method





How to assure global comparability for GOM ?

Sampling	+	Processing	+	Measurement	=	Result
Representative Appropriate Contamination for Stability	ree	selective trapping of GOM		Comparison to SI units or conventional scale		± uncertainty

VIM definitions:

Traceability id the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties."





New Measurement Methods

Reactive Mercury Active System (RMAS): membrane-based measurement system

- RM, GOM, and PBM
- Developed by Gustin team

Dual Channel Systems: automated system

- \circ RM, GOM
- Developed by Lyman and Gustin team
- MercOx dual channel system (Optoseven)
- $\circ~$ NOAA and others are developing other dual channel systems



Reactive Mercury Active System (RMAS)

Ion exchange membranes capture RM, GOM, or PBM

Low-cost, easy to use, rugged

1- to 2-week resolution

RM concentrations

➡ PBM and GOM concentrations

➡ RM chemistry

nstitute

→ PBM and GOM chemistry



RMAS Deployment Locations





RMAS Membrane Analyses

Total Hg Concentrations

- Digestion following EPA Method 1631
- Analysis by cold vapor atomic fluorescence spectroscopy

Tekran 2600-IVS (CVAFS)



Hg Chemistry

- Thermal desorption
- Individual Hg compounds desorb at characteristic temperatures







Dual Channel Systems (DCS)

Automated systems, with high temporal resolution for RM and GOM measurements

Uses a front end inlet to sample ambient air, that is split into two air streams within the system

 Quantify atmospheric Hg (total concentration or fractions) using Tekran 2537 or Lumex

Dual channel systems are being developed by several teams



Dual channel systems use membrane technology to rapidly measure oxidized Hg











Total Hg (A) – elemental Hg (B) = Oxidized Hg





Calibration Requirements

Developed calibrated methods MUST be

- Traceable to SI or an agreed standard
- Comparable (measurement uncertainty)
- Stable source of oxidized Hg over time
- Field-deployable
- Economical
- User-friendly

Inter-comparison of calibrators is/will be needed



Oxidized Hg Calibration Methods

Need a standard method for calibrating methods used to measure reactive Hg

- \circ Permeation tubes
- Diffusion
- Liquid standards
- o Plasma

Development of a calibration system that may be used when making ambient air measurements in the field • Several teams and institutions working toward this goal





Permeation Tubes

Permeation tubes can be used to calibrate oxidized Hg

Hg solid, emits oxidized Hg vapor through tube wall





Permeation Tube-Based Calibrator

Dual channel systems can quantitatively recover oxidized Hg compounds from our calibrator





Liquid evaporative gas generator developed by Optoseven/Mercx project OPEN ACCESS IOP Publishing Meas, Sci. Technol. 31 (2020) 034001 (14pr

Measurement Science and Technology

https://doi.org/10.1088/1361-6501/ab4d68

Dynamic calibration method for reactive gases

Saxholm Sari[®], Rajamäki Timo, Hämäläinen Jussi and Hildén Panu

VTT, National Metrology Institute VTT MIKES, Tekniikantie 1, FI-02150 Espoo, Finland





Calibration for GOM measurements

GOM generators: impurities of Hg⁰ (up to 5%)

Lumex: MercOx two channel analytical set-up





Oxidized Hg Hg filter generator ambient air ambient air lg filter Elemental Cell mercury Industrial fan channel PTFE **PYRO** RA-915F Pump Pump Hg Hg Suitable for on-line filter filter emission monitoring – high Hg concetrations! PC

Jožef Stefan Institute



sensors

Mercury

MerOx/Optoseven calibrator output time-trends through different concentration ranges



Jožef Stefan Institute Cold plasma GOM generation – traceability to NIST 3133 and 3177



Non-thermal or cold plasma

Atmospheric pressure and ambient T

Traceable quantity of Hg(0) in He gas





denuders

No detectable breakthrough of any Hg species

100

1,00

Relative intensity of released Hg 0,00 0,00 0,00 0,00

> 0,00 -100

Gačnik et al., Anal Chem. 2022, Under review

Thermogram - HgBr₂ vs HgCl₂

300 500 Temperature (°C) —н...

—Н...

700



USU DCS at Storm Peak Laboratory, CO

Detecting Hg oxidation events in air from the free troposphere

> Jožef Stefan nstitute





Tyler Elgiar working inside an automated calibrator

Comparison of Multiple Systems



Conclusions & Next Steps

Research teams are making progress toward development of oxidized Hg measurement and calibration methods

New measurement methods are demonstrating comparability

New calibrator method is demonstrating accurate measurements by the RMAS and dual channel systems

Next Steps

- Continued development and testing of accuracy, precision, robustness, and comparability of newly developed measurement and traceable calibration methods
- Traceability is a key to comparability!
- Harmonization of new methods and demonstration of comparability is urgently needed by global community (i.e., field inter-laboratory comparisons)



Acknowledgements

1

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Thanks to the undergraduate and graduate students working in the Gustin and Lyman labs that help keep our research moving forward.

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Thank you for your attention

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